PTO/PCT Rec'd 22 MAR 2002
09/914029

PIGMENTS BASED ON SILICA AND IRON OXIDE AND PROCESS FOR THE MANUFACTURE THEREOF

Field of the Invention

The present invention relates to the technical field of pigment manufacturing. Specifically, it deals with obtaining silica and iron oxide pigments useful in different industries and particularly in the ceramics industry. The silica component of these pigments would be obtained from microsilica or from fumed silica as the most characteristic feature of the invention.

Description of the state of the art

The natural pigments, silica - iron, have been known since ancient times for their chromophore properties. Extensively used in ceramics for colouring the mass, they provide a colour within the range of ochre - browns - oranges - reddish, on being introduced in high ratios which range from 2 to 12% by weight. However, they essentially lack homogeneity due to variations in the physico-chemical characteristics of the deposits.

Several efforts have been carried out trying to reproduce the features of this type of natural colorants, although these efforts have always come up against the limitation of achieving good quality products at a competitive cost relative to the market prices established for naturally occuring products.

In the prior developments there are different attempts to reproduce this type of colorants based on wet reaction processes, obtaining a gel, Fe_2O_3, $xSiO_2$, with a Fe_2O_3 content of 5 to 15% by weight, which must be submitted to a drying, calcination and milling process in order to obtain the product with an adequate quality.

In US patent 3,005,724 (1961), the starting product is a colloidal silica as a silica source, and a source of iron oxide, preferably iron sulphate, obtaining a suspension which is gelified by the addition of an alkaline solution. This gel is dried and calcinated at temperatures between 900

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and 1400º C and afterwards it is milled in order to obtain the pigment.

On the other hand, there are patents in which fumed silica is used to improve the features of the iron oxide synthetic pigments. In these cases, low silica ratios between 0.25 and 10 % of SiO_2 by weight are used, and it is used to improve the flowability and the coloration of the pigments in comparison with the synthetic iron oxides.

US patents 4,221,607 and 4,229,635, are disclosing processes for obtaining this type of iron oxide, starting from a solution of copperas as a source of iron oxide, to which a small proportion of silica is added (between 0.25 and 10% by weight) to obtain the iron oxide pigments with improved properties after a drying and calcination process. In US patent 4,221,607, the addition of silica is carried out before drying and calcination and an iron pigment is obtained which behaves better in the calcination process, while in US patent 4,229,635, the addition of iron is carried out after the calcination process and during a washing process of the colorant, before final drying and milling, obtaining a pigment with improved flowability.

References have not been found to the use of microsilica for the manufacture of silica-iron oxide pigments.

Brief description of the invention

The object of the present invention was to obtain inorganic pigments of the silica-iron oxide, X Fe_2O_3 and SiO_2 system, using microsilica or fumed silica as the silica source, along with the process for industrial obtention of said pigment. The obtained pigments may have a of red - orange hue colouration, above all when used in the manufacture of ceramic products of low porosity such as porcelain stoneware. They are a competitive alternative, in terms of quality and cost, to natural materials such as Thiviers stoneware, which are currently used. The presentation of the product is in the form of a micronised powder. The product can be incorporated into the base

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composition through a direct dispersion mechanism without the need for milling.

Detailed description of the invention

The colorants object of the invention consist mainly of mixtures of silicon oxide (silica), in ratios that range between 70 and 98 % by weight, and iron oxide, in different ratios, referred to a mixture of SiO_2 and Fe_2O_3.

This invention uses microsilica or fumed silica as the silicon oxide source. Which is basically obtained as a by-product by condensation of the gases evolved during the process of manufacturing silicon metal (electric arc melting) and alloys of silicon and other metals. Said product is characterised by its high content in silica (greater than 90 % expressed as SiO_2) and by its extremely fine particle size (around 100 nm).

As a source of iron oxide, red and/or yellow iron oxide (natural and/or synthetic) can be used, or salts and/or complexes of iron that can be oxidised and/or decompose during the calcination process to provide iron oxide.

Small quantities of additive can be added to these basic mixtures to improve the features of the colorant and/or to modify its coloration.

The resulting colorants are pigments of a red-orange colour which can be used for colouring all sorts of materials, preferably ceramic materials, and specially ceramic masses that provide porcelain stoneware type low porosity ceramic materials.

Depending on the composition, source of iron oxide, conditions of subsequent firing and treatment to which the colorant is submitted, a wide range of colours can be obtained within the red-orange tones.

In essence, the silica provides a protective coating layer for the iron oxide particles, protecting against external aggressions such as temperature, atmosphere and/or attack by other compounds. This protective layer ensures that the iron oxide processed in this way, remains more

stable during its use in ceramic compositions that are submitted to high temperatures during their manufacture.

These colorants of silica-iron are obtained by calcination of mixtures of raw materials at high temperatures, forming a pigment with tridymite and/or crystobalite structure in which the iron oxide is incorporated with hematite structure. The tridymite or crystobalite are formed by calcination of the amorphous silica, obtaining a stable structure or another one, depending on the firing conditions and on the present additives and impurities.

method

The different compositions of raw material can be prepared through dry or wet processes. In the dry process, the mixture of raw materials is carried out in a mill or a blender. The resulting mixture may optionally be granulated to facilitate its handling (transport, dosing...). In the wet process, a suspension in water of the raw materials is prepared by milling and dispersion, drying the mixture in an atomisation process, in which an agglomerated material suitable for subsequent processing is obtained.

These mixtures of raw materials, more or less agglomerated, may optionally pass through a prior drying stage, to then proceed to calcination (thermal treatment at high temperature in which the different physico-chemical transformations that convert the material into its finished state will take place). Said calcination may be carried out in different oven types at temperatures comprised between 800 and 1300º C, depending on the features of the silica, the source of iron oxide and the used additives.

In some cases, a prior calcination may be effected, at a lower temperature to suitably prepare the raw materials for their subsequent reaction. In this stage, if necessary, the present organic material and the iron oxide are oxidised and/or the raw material acting as a source of iron oxide is decomposed.

After calcination the product is submitted to a particle size reduction step to provide a more homogeneous

colour. Said operation is preferably carried out in a dry milling installation, with dynamic classification which permits to assure that more than 99 % of the particles are smaller than 40 micrometers.

Examples

<u>Example 1</u>

87 kg of microsilica and 13 kg of synthetic red iron oxide are milled in a silex-ball mill for 4 hours with 50 litres of water. The suspension obtained is dried and the granulate obtained calcinated at a maximum temperature of 1050º C for three hours. A red coloured product is obtained, which is milled in a mill with alumina balls in dry conditions, until 99 % of the particles are smaller than 40 microns. This colorant, added to a standard composition of porcelain stoneware in a ratio of 5 % by weight, provides fired pieces with Hunter-LAB chromaticity coordinates of L=38.0 a=15.6 b=7.4.

<u>Example 2</u>

346 kg of microsilica and 72 kg of synthetic red iron oxide are granulated in an intensive granulation machine with 80 litres of water. The granulate obtained is dried and calcinated at 1025º C for 6 hours at this maximum temperature. A reddish coloured product is obtained, which is milled in the same way as example 1. The chromaticity coordinates that are obtained are L=40.3, a=15.0 and b=7.3.

<u>Example 3</u>

94 kg of microsilica and 6 kg of synthetic red iron oxide are processed in the same way as in example 1. The chromaticity coordinates that are obtained are L=43.5, a=17.2 and b=8.5.

<u>Example 4</u>

A suspension is prepared with 65.8 kg of microsilica, 34.2 kg of ferrous sulphate ($FeSO_4 \cdot 7H_2O$) and 75.0 kg of water in a silex-ball mill. The milling lasts 4 hours. The suspension is dried and a granulate obtained that is pre-calcinated to decompose the sulphates and to oxidise the iron oxide and then the mixture is calcinated at 1100º C.

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The chromaticity coordinates that are obtained for the fired pieces prepared with 5% by weight of colorant are L.43.0, a=16.6 and b=10.5.

Description of the figures

Figure 1. Block diagram of the manufacturing process used.

1. Microsilica
2. Source of iron oxide
3. Milling
4. Agglomeration
5. Pre-calcination
6. Calcination
7. Cooling
8. Blending
9. Dry milling
10. Blending
11. Sacking